

1922
W432

**REACTIONS OF COUMALINIC ACID AND
PREPARATION OF ITS CHLORIDE**

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

THE SIGHTS OF THE MOUNTAINS

ENTITLED ACTIONS OF COUALLYLIC ACID AND THE PREPARATION
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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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Acknowledgment.

The author wishes to express his sincere thanks and gratitude to Dr. B. L. Toulon for his kind suggestion and helpful encouragement during this work.

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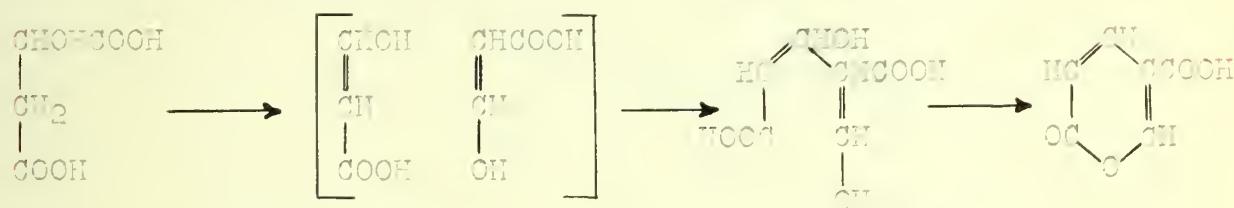
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HISTORICAL

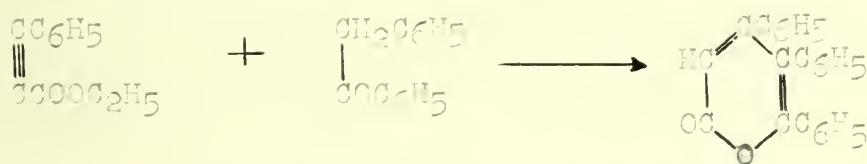
Alpha Pyrones

Alpha pyrones have been prepared by several general methods. First, by the action of concentrated sulphuric acid on an aldehyde acid or a ketonic acid. For example, coumarinic acid (I) was prepared in the following manner:

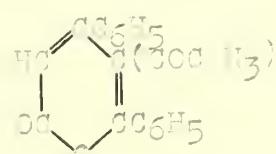
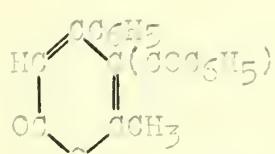


From acetobutyric acid, 2-hydroxyacetic acid (IV) was obtained and in a similar manner acetodicarboxylic acid gave citra-coumarinic acid (III).

Second, by the addition of β -ketonic esters and certain ketones to esters of acetylenic acids. Desoxybenzoin added to ethyl phenylpropionate giving 4:5:6 triphenyl alpha pyrone (XV).

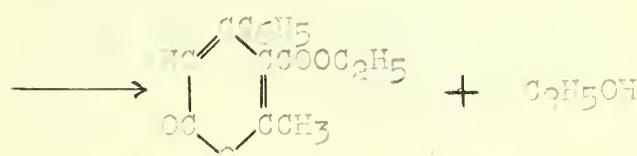
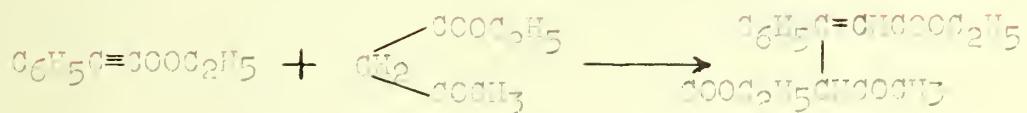


Acetylacetone and benzoylacetone in like manner gave respectively 4-phenyl-6-methyl-5-aceto alpha pyrone (XVI) and 4-phenyl-5-benzoyl-6-methyl alpha pyrone (XVII) or 4:6 di-phenyl-5-acetyl alpha pyrone (XVIII). In the latter case the formula of the compound is one of the following:



* See table for references.

The following equation expresses the reaction between ethyl acetacetate and ethyl phenylpropionate.



Ethyl-4-phenyl-6-methyl alpha-pyron-5-carboxylate (VIII).

The halogen derivatives of the alpha-pyron compounds were obtained by direct chlorination or bromination of the acids and esters. In some instances, as for example, in carrying out the chlorination of ethyl coumalate, solvents were used such as carbon tetrachloride saturated with chlorine.

Coumalin (XII) the simplest of the alpha-pyrones was prepared by H. V. Peckham by the dry distillation of mercurous coumalinate in an atmosphere of hydrogen.

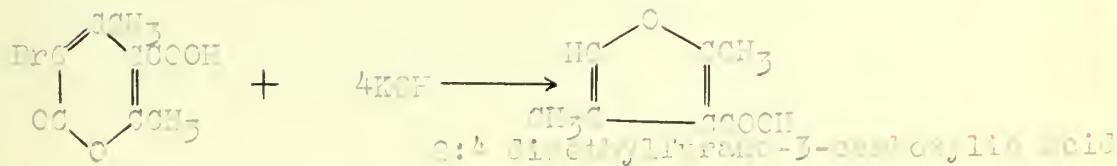
I		M.P. 205-210	Soluble in methyl alcohol, acetic acid, ether, water and acetone.	Ber. 17, 2334
II		M.P. 227-228	Soluble in alcohol, acetic acid, water, and acetone.	J.C.S. 1901 T.Pt. 2, 1280
III		M.P. 185 Turns dark at 150	Soluble in water and alcohol.	Annalen 261 190-208
IV		M.P. 50		Annalen 261 190-202
V		M.P. 74 B.P. 60 178-8	Soluble in ether, alcohol, acetone and water.	Annalen 264 271
VI		M.P. 36 B.P. 262-265	Soluble in ether, alcohol, acetone and water.	Annalen 264 261-309
VII		M.P. 59-60	Soluble in water, and in most organic media.	J.C.S. 1901 T.Pt. 2 1280

VIII		M.P. 187-190	Soluble in acetic acid, alcohol and ether.	Ber. 37, 3829-30
IX		M.P. 134-136	Soluble in chloroform, acetone, acetic acid, and benzol.	Ber. 17, 2396-2399
X		M.P. 176	Soluble in ether, alcohol, chloroform and glacial acetic acid	Ber. 17, 2396-2399
XI		M.P. 161-162	Soluble in alcohol and benzene.	Ber. 26, 746-747
XII		M.P. 72		Ber. 35, 782-790
XIII		M.P. 94-95	Soluble in alcohol	Annalen 321 367-384
XIV		M.P. 66-68	Soluble in ether, alcohol, acetic acid and water.	Ber. 27, 841-850

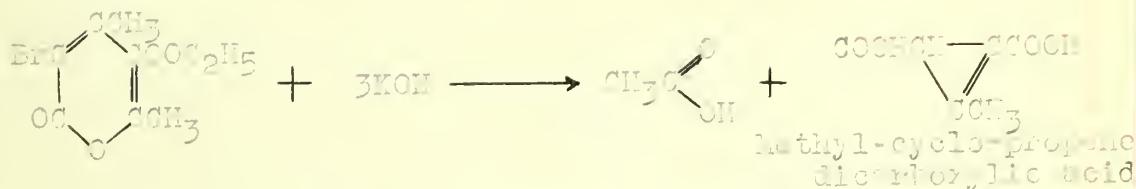
XV		M.P. 245-246	Soluble in glacial acetic acid. Insoluble in water or alcohol.	J.C.S. 1910 T. 457.
XVI		M.P. 128		J.C.S. 1899, T. 411.
XVII		M.P. 143-144		J.C.S. 1899, T. 411
XVIII		M.P. 104		Ber. 35, 782-790
XIX		B.P. 206-9d M.P. 5 B.P. 30 120	Miscible with all ordinary solvents.	Annalen 264 261-309

THEORETICAL

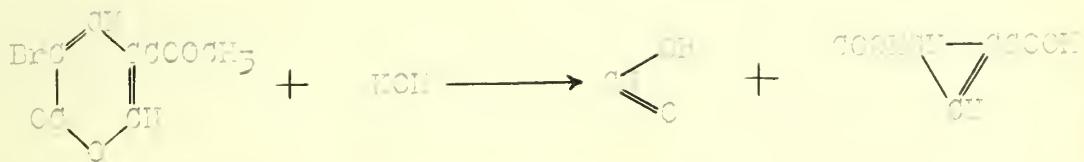
Trans Foist treated bromo-isoderyltracetic acid with potassium hydroxide and obtained a furane derivative.



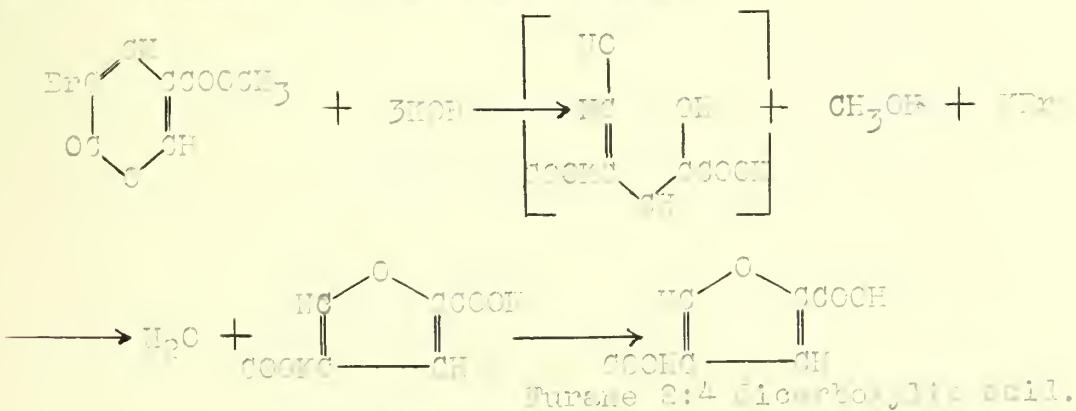
He then treated ethyl-bromo-isoderyltracetic ester with potassium hydroxide and obtained a cyclo-propene derivative.



This led him to investigate a simpler alpha-pyrone, methyl-bromo-cumulinate expecting to obtain a cyclo-propene compound similar to that obtained from the ethyl-bromo-isoderyltracetic ester.



Instead he obtained a furane derivative.



Since methyl-chlorocumulinate (IX) prepared by

v. Paulmair and Kille, was never converted either into the cyclo-propene derivative nor into the furan derivative. There existed a curiositatem to which of the two derivatives it would give on treatment with potassium hydride, which therefore led to this investigation.

EXPERIMENTAL

Comalinic acid:-H.v.Pechman prepared comalinic acid (I) by heating malic acid (50 grams) on the water bath with a mixture of (75 grams) concentrated sulphuric acid and (75 grams) fuming sulphuric acid containing 10-12 per cent sulphur trioxide. When the evolution of carbon dioxide ceased to 1 1/2-2 hours, the solution was carefully mixed with ice (200 grams) and kept over night. The precipitated acid was separated by filtration, washed with ice water until it was free from sulphuric acid and then dried on porous plates. The acid in the mother liquors and washings was extracted by shaking sometimes with ether. The total yield of the crude product was about 80 per cent, but it contained fumaric acid and traces of trimalic acid. It was purified by dissolving in water between 70-80 degrees, shaking the solution with animal charcoal, and then extracting the acid with ether. It crystallized from free methyl alcohol and glacial acetic acid in colorless prisms, and on heating turns red at 200 degrees, and melted between 205-210 degrees with decomposition. It boiled at 213 degrees under a pressure of 100 mm. with partial decomposition.

As fuming sulphuric acid containing 10-12 per cent sulphur trioxide could not be obtained in the laboratory, fuming sulphuric acid containing 7 per cent sulphur trioxide was used and the amount per 50 grams of malic acid was calculated. A mixture of (40 grams) concentrated sulphuric acid and (110 grams) of fuming sulphuric acid 7 per cent sulphur

trioxide was used, and procedure as given by v. Dechman was carried out. An 83 per cent yield of crude product was obtained but could not be purified according to v. Dechman's method. Different methods of purification, and such solvents as alcohol, chloroform, acetone, ether, petroleum ether and ethyl acetate were tried but colorless prisms could not be obtained.

By dissolving the crude acid in hot glacial acetic acid and allowing it to cool the coumarinic acid crystallized. The crystals had a yellowish color, and no definite shape. The yield of pure acid was 63 per cent.

Methyl Coumarinate.

Methyl coumarinate (7) was prepared by H.V. Peckham by adding to one part of the acid 2 parts of sulphuric acid and heating for 15 minutes. Then adding one part of methyl alcohol and refluxing for one hour on a water bath. After cooling it was poured into water and filtered to remove from the water and trichloro-ether. The filtrate was extracted 10 times with ether, dried, the solution evaporated and the precipitating substance crystallized in long needles. It was recrystallized from hot water, ether or ligroin. The yield was 75 to 85 percent of the weight of acid used, and the melting point was from 73-74 degrees.

Four methods of preparing the ester were tried.

- (1) The method used by H.V. Peckham; (2) By passing dry hydrogen chloride into a mixture of acid and methyl alcohol; (3) by treating the silver salt of the acid with methyl iodide; (4) by passing methyl alcohol vapors through a mixture of acid, sulphuric acid and methyl alcohol.

(1) After following H. Peckham's method of preparation, methyl coumarinate melting from 72-73 degrees was obtained. The best yield obtained in a half dozen trials was 40 percent of the weight of acid used.

(2) One part of the acid was added to one part of methyl alcohol and dry hydrogen chloride was passed in until the solution was completely saturated. The solution was poured into water and filtered. The filtrate was extracted 10 times with ether, washed with a dilute solution of sodium carbonate

then dried with calcium chloride. The solution was evaporated and a brown, sticky substance remained that could not be crystallized. Later it was concluded that if the mass were distilled under diminished pressure methyl coualinate would be obtained.

(3) 10 grams of coualinic acid was dissolved in ammonia water, made almost neutral with nitric acid and silver nitrate added. The silver salt was filtered off and placed into a flask connected to a reflux condenser. Ether and methyl iodide were added respectively and the solution was permitted to reflux for three hours. After evaporating the ether solution a brown mass remained which could not be crystallized.

(4) To 30 grams of coualinic acid and 6 cc. sulphuric acid, 60 cc. of methyl alcohol was added. Absolute methyl alcohol vapors were passed through the mixture removing the water formed in the reaction. When the reaction was complete, the solution was cooled, poured into water and the oil layer was separated from the water layer. The water layer was extracted twelve times with ether, made neutral by washing with a dilute solution of sodium acid carbonate, dried with calcium chloride and the ether evaporated. The resulting material was distilled under diminished pressure. Methyl coualinate distilled over between 170-180 degrees and 60 mm. Melting point of the ester, 73-74 degrees. The oil layer of distillation gave 6 grams of methyl coualinate. Total yield of ester was 42 per cent of the weight of acid used.

Methyl-chlorocoumalinate

To 30 grams of pure methyl coumalinate (V), the calculated amount of carbon tetrachloride saturated with 7-8 per cent chlorine was added and allowed to stand at room temperature. After two or three days hydrogen chloride started to be given off and crystals formed. The crystals were separated, and washed with ether. The crude product (25 grams) was then recrystallized from alcohol. 17 grams of pure chloro-ester melting, 134-136 degrees was obtained.

This method was tried about a dozen times with 5 to 10 grams of pure methyl coumalinate and the best yield obtained was one gram of pure methyl-chlorocoumalinate for every 10 grams of methyl coumalinate. The crude product obtained melted between 94-103 degrees, but after recrystallizing three times from alcohol, a pure product melting, 133-135 degrees was secured.

Sulphuryl chloride was tried instead of carbon tetrachloride but the yield was not increased.

* Furane 2:4 dicarboxylic acid.

Methyl-bromocoumalinate (5grams) were mixed in a cold solution containing (10 grams) potassium hydroxide in (20 grams) of water. It was heated for twenty minutes, allowed to cool and then neutralized with sulphuric acid. The whole mass was placed on a water bath to dry. The brown mass remaining was extracted with acetone. After vaporizing the acetone a brown mass remained which was washed with ligroin and recrystallized from hot water. The yield was 3.7 grams, melting at 260 degrees.

When 2 grams of methyl-chlorocoumalinate was obtained, the procedure as given above was followed through. The brown mass obtained after vaporizing the acetone was insufficient to carry the operation any further. Lack of time prevented the preparation of more methyl-chlorocoumalinate; thus the problem had to be left without a definite conclusion.

SUMMARY

Quinolizic acid was prepared in better yields than that recorded in the literature.

The acid was identified using sulphuric acid as catalyst.

Difficulty was experienced in preparing ethyl-chloro-cominate in sufficient quantities to work with. One experiment, ethyl-chloro-cominate plus potassium hydroxide gave no solid product.

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